

FORM PTO-1390 (Modified)  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

4297

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/601062

INTERNATIONAL APPLICATION NO.  
PCT/IL99/00045 ✓INTERNATIONAL FILING DATE  
25 January 1999 ✓PRIORITY DATE CLAIMED  
26 January 1998 ✓

TITLE OF INVENTION HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE  
PYROLYSIS TREATMENT AND HALOGENATION OF MULTI-ELEMENT WASTE ✓

APPLICANT(S) FOR DO/EO/US

Ariel ROSENBERG ✓

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

AN INFORMATION SHEET

A COPY OF THE SPECIFICATION, CLAIMS, DRAWING

THE FEE CALCULATION MUST BE BASED ON THE CLAIMS CONTAINED  
IN THE PRELIMINARY AMENDMENT.

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>09/601062</b> )	INTERNATIONAL APPLICATION NO. PCT/IL99/00045	ATTORNEY'S DOCKET NUMBER 4297
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20. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :					
<input checked="" type="checkbox"/>	Search Report has been prepared by the EPO or JPO .....	\$840.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) .....	\$670.00			
<input type="checkbox"/>	No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) .....	\$760.00			
<input type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$970.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) .....	\$96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =				840.	<del>\$0.00</del> -
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	41 - 20 =	21	x \$18.00	378.	<del>\$0.00</del> -
Independent claims	2 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				1218.	<del>\$0.00</del> -
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				\$0.00	
SUBTOTAL =				1218.	<del>\$0.00</del> -
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30			+	\$0.00	
TOTAL NATIONAL FEE =				1218.	<del>\$0.00</del> -
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				1218.	<del>\$0.00</del> -
				Amount to be: refunded	\$
				charged	\$

- ☐ A check in the amount of \_\_\_\_\_ to cover the above fees is enclosed.
- ☒ Please charge my Deposit Account No. 01-1944 in the amount of \$1218.00 to cover the above fees. A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 01-1944 A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Anderson, Kill & Olick, P.C.  
1251 Avenue of the Americas  
New York, NY 10020-1182

SIGNATURE

Eugene Lieberstein

NAME

24645

REGISTRATION NUMBER

July 26, 2000

DATE

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY  
STATUS (37 CFR 1.9(f) AND 1.27 (b)) - INDEPENDENT INVENTOR**

Docket No.  
4297

Serial No.  
09/601,062

Filing Date  
July 26, 2000

Patent No.

Issue Date

Applicant/ **Ariel ROSENBERG**  
Patentee:

Invention: **HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE PYROLYSIS TREATMENT  
HALOGENATION OF MULTI-ELEMENT WASTE**

As a below named inventor, I hereby declare that I qualify as an independent inventor as defined in 37 CFR 1.9(c) for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, to the Patent and Trademark Office with regard to the invention entitled above and described in:

- ☐ the specification to be filed herewith.  
☒ the application identified above.  
☐ the patent identified above.

I have not assigned, granted, conveyed or licensed and am under no obligation under contract or law to assign, grant, convey or license, any rights in the invention to any person who could not be classified as an independent inventor under 37 CFR 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☒ No such person, concern or organization exists.  
☐ Each such person, concern or organization is listed below.

\*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities (37 CFR 1.27)

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF INVENTOR Ariel ROSENBERG

SIGNATURE OF INVENTOR 

DATE: 10/10/00

NAME OF INVENTOR \_\_\_\_\_

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: \_\_\_\_\_

NAME OF INVENTOR \_\_\_\_\_

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DATE: \_\_\_\_\_

NAME OF INVENTOR \_\_\_\_\_

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: \_\_\_\_\_

09/601062<sup>PTO</sup>

534 Rec'd PCT/PTC 26 JUL 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN THE MATTER OF:

APPLICANT: Ariel ROSENBERG

ORDER/DOCKET NO. 4297

FOR: HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE  
PYROLYSIS TREATMENT AND HALOGENATION OF MULTI-ELEMENT WASTE

JULY 24, 2000

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents  
and Trademarks  
Washington, DC 20231

S I R:

In an effort to reflect the amendments made in the International Phase of this application before the European Patent Office, Applicants would like to make the following amendments in U.S. style so as to be certain to reflect properly that which was amended during the International Phase:

IN THE SPECIFICATION

Page 4, insert the following paragraphs between lines 2 and 3 as follows:

- - WO 97/29214 discloses a process for the separation of metals from incinerated garbage residue and slag, the residue and slag from garbage incinerated pyrolysis being heated at over 650°C under reducing conditions together with substances containing chlorines or chlorides, such as flue gas cleaning residues, CaCl<sub>2</sub> from the production, cooking salt, organic solvents or electroplated sludge containing chlorine, whereupon copper chlorides and volatile heavy metal chlorides are drawn off in the gas phase.

USP 4,317,800 discloses a process for reducing environmental pollution resulting from disposal of waste-containing halogenated hydrocarbons by some simultaneous treatment with used metal and/or metal scrap at elevated temperatures. The halogenated hydrocarbons are pyrolyzed, and the resulting hydrogen halide-containing gas is brought into contact with the metal at elevated temperatures so as to form halogenites that are volatile under the conditions supplied.

WO 95/33686 discloses a method for extracting metals from metal-containing materials, especially waste, by pyrohydrolysis. The metal-containing materials are made to react at 700-1100°C, with gas a composition comprising 25 - 45% water vapor, 0.1% carbon dioxide, 2 - 20% hydrogen chloride and 0-15% carbon monoxide, the remainder being nitrogen and possibly oxygen, and the metals are extracted in the form of volatile metal chlorides.

WO 95/22373 discloses a method for removing pollutants consisting of heavy metals and toxic elements from fly ash and few purification residues resulting from waste incineration. The waste is subjected to chlorination, thermal treatment, sulfuration for the twofold purpose of the removal and concentration of a fraction containing heavy metals and toxic elements. - -

#### IN THE CLAIMS

Please cancel claims 1 - 43 and substitute therefore claims 44 - 84 as follows:

- - 44. A highly efficient recovery process for the treatment of multi-element wastes which comprises the steps of:

- a) a primary heat treatment of the waste in the presence of a controlled amount of oxygen;
- b) after the completion of said heat treatment, halogenation of the product of said heat treatment by treatment with chlorine, bromine or a mixture thereof, in the presence of a halogenation catalyst; and

c) separation of the metal halide products of said halogenation.

45. A process according to claim 44 in which said multi-element waste is unsorted.

46. A process according to claim 44 in which the waste to be recovered is such that has been mechanically prepared in a process which includes any one or more of the steps of shredding, crushing, milling and briquetting.

47. A process according to claim 44 in which said primary heat treatment further comprises mechanically agitating the waste during said treatment.

48. A process according to claim 44 in which the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

49. A process according to claim 44 in which the primary heat treatment is carried out under atmospheric pressure or higher pressure, optionally in the presence of gases, preferably hydrogen, capable of cracking the organic or inorganic material.

50. A process according to claim 44 in which at least a portion of the heat energy afforded in the primary heat treatment is used in the halogenation reaction.

51. A process according to claim 44 in which at least a portion of the product of the primary heat treatment is used as a catalyst in the halogenation reaction.

52. A process according to claim 51 in which said products to be used as catalysts are selected from the group which consists of carbon, bromine, carbon, CO, CO<sub>2</sub> and SO<sub>x</sub> and NO<sub>x</sub> compounds.

53. A process according to claim 44, wherein the primary heat treatment is performed in an oven.

54. A process according to claim 53, wherein said oven is at a temperature of less than about 1000°C.

55. A process according to claim 44, wherein the primary heat treatment is performed in a metallic molten bath.

56. A process according to claim 55, wherein said molten bath is at a temperature of between 500°C and 1600°C.

57. A process according to claim 44 which further comprises a secondary heat treatment comprising heating the gaseous flow which results from the primary heat treatment to a temperature of more than 1200°C.

58. A process according to claim 44 in which said halogenation step further comprises mechanically agitating the waste during said step.

59. A process according to claim 44 in which the halogenation reaction is performed at a temperature of between ambient temperature and 1500°C.

60. A process according to claim 44 in which the halogenation reaction is performed at a temperature of between 300°C and 1500°C, and preferably between 700°C and 750°C.

61. A process according to claim 44 in which the waste comprises a substantial percentage of any of the metals selected from the group which consists of Ag, Pt and Pd, and the halogenation reaction is performed by using a mixture of bromine and chlorine.

62. A process according to claim 61 in which said mixture of chlorine and bromine comprises between 93% and 99% chlorine and the remainder is bromine.

63. A process according to claim 44 in which at least a portion of the excess halogen gas remaining from the halogenation reaction is recycled back to the halogenation chamber.



64. A process according to claim 44 in which the separation of the metal halides is by means of any one or more of the group selected of gaseous or liquid fractional deposition, distillation, fractional distillation, filtration, selective chemical vapor deposition, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution and selective extraction.

65. An apparatus for a high efficient recovery process for the treatment of multi-element wastes, which comprises:

I) a primary heat treatment chamber (3);

II) a halogenation chamber(9); and

III) a separation unit (11 to 15) connected to said halogenation chamber;

IV) said primary heat treatment chamber comprising a waste inlet (2), a flue-gas outlet (20) and means of heating; and

V) said halogenation chamber comprising a means of heating, a halogen compound inlet (10) and an outlet (16).

66. An apparatus according to claim 65 in which the flue-gas outlet of said primary heat treatment chamber is connected to said halogenation chamber by means of a conduit, which comprises a valve.

67. An apparatus according to claim 65 in which said separation system comprises one or more of the units selected from the group which consists of fractional deposition unit, distiller, filter, settler, selective chemical vapor deposition unit, selective oxidation chamber, selective halogenation chamber, evaporation chamber and selective dissolution unit or any combination thereof.

68. An apparatus according to claim 67, wherein the separation system comprises

fractional deposition unit or selective chemical vapor deposition unit.

69. An apparatus according to claim 65 in which said separation system is a gaseous fractional deposition system; the inlet of which is connected to the outlet of said halogenator by means of a conduit.

70. An apparatus according to claim 69 in which the outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber, and said pipe comprises a one-way valve in the direction from the fractional deposition system to the halogenation chamber.

71. An apparatus according to claim 65 which further comprises a secondary combustion chamber (5) and a heat exchanger (8); said secondary combustion chamber comprising a means of heating, a gas inlet, an air inlet, and a flue gas outlet; said gas inlet of said secondary combustion chamber being connected by means of a conduit to the flue gas outlet of said primary heat chamber; said heat exchanger comprising an inlet and an outlet; the flue gas outlet of said secondary combustion chamber being connected by means of a conduit to the inlet of said heat exchanger.

72. An apparatus according to claim 71 which further comprises a scrubber, a filter, a blower and a stack; said scrubber comprising an inlet and an outlet; the outlet of said heat exchanger being connected by means of a conduit to the inlet of said scrubber; said filter comprising an inlet and an outlet; the outlet of said scrubber being connected by means of a conduit to the inlet of said filter; said blower comprising an inlet and an outlet; the outlet of said filter being connected by means of a conduit to the inlet of said blower; said stack comprising an inlet and an outlet; the outlet of said blower being connected by means of a conduit to the inlet of said stack.

73. An apparatus according to claim 72, wherein the scrubber and the filter are connected to the halogenation chamber by means of conduits to recycle material recovered and collected by said scrubber and filter to said halogenation chamber.

74. An apparatus according to claim 72 in which said filter is selected from the group which consists of fabric filter, electrostatic filter, and high temperature filter.

75. An apparatus according to claim 67 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter doser, and sludge feeder which are connected to the primary heat treatment chamber providing that the outlet of the unit connected to the primary heat treatment chamber is connected to the inlet of said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly in any combination and/or order and are connected so by means of conduits.

76. An apparatus according to claim 65 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter, doser and sludge feeder which are connected between the primary heat treatment chamber and the halogenation chamber; providing that the outlet of the unit which is connected to the halogenation chamber is connected to the inlet of said halogenation chamber by means of a conduit; further providing that the outlet of the primary heat treatment chamber is connected to the inlet of the unit which is connected to said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly in any combination and/or order and are connected so by means of conduits.

77. An apparatus according to claim 65 in which said primary heat treatment chamber further comprises a means of agitating material.

78. An apparatus according to claim 77 in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

79. An apparatus according to claim 65, wherein the primary heat treatment chamber comprises a pressurized vessel.

80. An apparatus according to claim 65 in which said halogenation chamber further comprises a means of agitating material.

81. An apparatus according to claim 80 in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

82. An apparatus according to claim 65, wherein the halogenation chamber comprises a pressurized vessel.

83. An apparatus according to claim 65 in which the primary heat treatment chamber is placed horizontally, vertically or at any other advantageous angle.

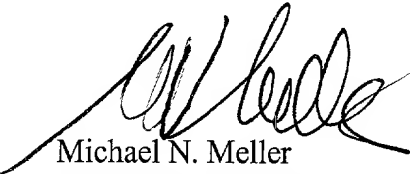
84. An apparatus according to claim 65 in which the halogenation chamber is placed horizontally, vertically or at any other advantageous angle. - -

REMARKS

In an effort to put this application into condition for early examination before the USPTO Examiner, Applicant hereby incorporates into the specification as originally filed in the European Patent Office, the amendments made during the course of the international examination as well as substitute a new set of claims for the ones with this case as originally filed.

It is believed that with these amendments the application is in favorable condition for examination by the U.S. Examiner and its early allowance.

Respectfully submitted,



Michael N. Meller  
Registration No. 20779

ma0724ro.amd

Anderson, Kill & Olick, P.C.  
1251 Avenue of the Americas  
New York, NY 10020-1182  
212/278-1000

534 Rec'd PCT/PTC 26 JUL 2000

HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE PYROLYSIS TREATMENT AND HALO-  
GENATION OF MULTI-ELEMENT WASTEFIELD OF THE INVENTION

The field of the present invention is processes for treating and recovering a large variety of types of wastes via chemical treatment.

BACKGROUND OF THE INVENTION

The present recovery and recycling industry must use a defined feed stock as raw material in order to be processed. As a result, the recovery industry must spend huge resources in sorting its wastes storing and warehousing. This is the main reason for the small quantity of waste which is actually being recycled, and the huge amount which is being dumped with catastrophic environmental effects.

Examples of the above are known and obvious, such as special scrap collectors, scrap yard dealers, for each segment of the industry - copper, aluminum, iron, steel, stainless steel, noble metal etc. in the recycling industry on the one hand, and the unlimited amount of waste being dumped by the society every day, on the other hand

However, the recycling industry is dedicated mainly to the industrial waste, which is well sorted and defined to each element. In the event that

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the scrap is made of different elements or metals, cheap labor is needed in order to dismantle the different components to the different metals. Examples are found in ship scrap, aircraft, cars and municipal waste. The main problem is, that this process requires cheap manpower that have to work in difficult and hazardous conditions. It has been proven in the developed countries, that manual or automated sorting and dismantling systems are usually not economically feasible and are therefore not a valid solution for treatment of most of the mixed waste.

Indeed many industries do address this issue by constructing equipment which makes recycling easy by use of the dismantling methods, such as used in the automobile industry etc. However, due to the use of many complex materials and the sophistication of parts it becomes almost impossible to re-use these parts or repair them.

The only system that treats unsorted waste, to any degree is the Municipal Incineration system, and even then, the waste must not be contaminated by industrial or Hazardous waste. In this system the waste is being introduced into furnaces and incinerated at elevated temperatures, where hot gases usually produce steam and or electricity. This system actually recovers only the energy of the organic matter via oxidation - incineration. All the inorganic waste remains as ash or sludge and is usually placed in a controlled landfill.

There are some other systems that have been developed to recover identified elements from identified feed stock - waste, via different systems, such as molten metals, extraction or chlorination methods. For example, Adelman et al (Proc. Iowa Acad. Sci. (1980) 87 (4), pp129-133) discloses the production of aluminum chloride and silicon chloride from fly ash. In this system recovery of Al, Si, Fe, and Ti via chlorination reaction in a gas fluidized bed reactor is used, to convert the metal in the fly ash to volatile metal chlorides. The best yields are achieved when CO and fluid coke are used as reduction agents. Typically 0.5 - 2 hours of chlorination at temperatures of 750 - 900 degrees to produce volatile metal chlorides.

Burnet et al. (Univ. Ky., Inst. Min. Miner. Res., [Tech Rep.] IMMR (1997), IMMR 32-M4-77, Proc. - Ky. Coal Refuse Disposal Util. Semin., 3rd 83-8) discloses a high temperature chlorination method of recovering  $Al_2O_3$  from the non-magnetic fraction of fly ash, in which the non-magnetic fraction of fly ash is mixed with C and chlorinated in a fixed bed. The residual Fe in the ash can be removed as volatile Fe chloride at 400-600°C, with very little Al and Si reaction. The temperature is then raised to 850-950°C where a mixture consisting mostly of volatile Al and Si chloride forms. When the vapors are cooled, solid  $AlCl_3$  condenses at 120-50°C. The  $SiCl_4$  remains in a vapor state due to its low condensation temp. The  $SiCl_4$  can



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be easily decomposed to form  $\text{SiO}_2$  and  $\text{HCl}$  from which the  $\text{Cl}$  is recycled.

Most wastes contain more than one element and several unknown contaminants. Most wastes contain both organic and non-organic elements.

The organic waste materials are in most cases a mixture of various chains of molecules together with various elements incorporated, as well as other non-organic materials, and are usually difficult in recycling, and they create environmental problems.

Chlorination of organic material can produce hazardous, toxic and cancerous elements.

It is a purpose of the present invention to provide a process for destruction of hazardous and/or toxic industrial waste in which the toxic and/or the hazardous compound waste is reduced into less toxic, or non toxic material, and/or less hazardous or non hazardous material, and the size and quantity of said waste is also reduced.

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It is a further purpose of the present invention to provide a self-catalytic process in which the matter that exists in the compounded waste is converted and used as a catalyst in a subsequent reaction.

It is a further purpose of the present invention to provide an energy recycling process in which the energy produced by one chemical reaction is consumed in a subsequent chemical reaction.

It is a further purpose of the present invention to provide a wide range recycling process in which almost any waste can be treated: organic, non-organic, metallic or non-metallic, sorted or even unsorted.

It is a further purpose of the present invention to provide a recycling process suitable for recovering the basic elements of the waste introduced thereto, thus obtaining valuable and useful materials.

### SUMMARY OF THE INVENTION

The present invention relates to a high efficient recovery process for the treatment of multi-element wastes which comprises the steps of:

- a) heat treatment of the waste in the presence of a controlled amount of oxygen;
- b) halogenation of the product of step "a"; and
- c) separation of the metal halide products of step "b".

The term "carbonization" used herein is defined as an operation in which organic material is subjected to high temperature in the presence of a limited amount of oxygen, resulting in the decomposition of said material, and affording, *inter alia*, carbon, CO and CO<sub>2</sub>.

The heat treatment described in the above step "a" may be referred to hereinafter as "primary heat treatment".

Optionally, when necessary, the raw waste is mechanically prepared in a process which includes any of the steps of shredding, crushing, milling and briquetting, prior the step of primary heat treatment.

Preferably the primary heat treatment is performed at a temperature of less than about 1000°C.

Preferably, during the primary heat treatment, the waste is agitated.

Preferably, the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

According to another embodiment of the present invention, the primary heat treatment is carried out under atmospheric pressure or higher pressures, optionally in the presence of gases, preferably hydrogen, capable of cracking the organic or inorganic material.

Preferably, the halogenation reaction is conducted with mechanical movement between the gaseous halogen and the waste, as fixed fluidized bed vibrating or in walking grid or in rotary kiln.

Preferably, the halogenation reaction is a chlorination reaction, a bromination reaction or a combined chlorination-bromination reaction, and more preferably a chlorination reaction.

Preferably, the halogenation reaction is performed at a temperature in the range between ambient temperature and 1500°C, more preferably between 700°C and 750°C.

Optionally, the halogenation temperature may vary according to the boiling or sublimation point of the metal halide products, as will be hereinafter explained.

Preferably, the separation of the halide products (step "c" above) is by means of any one or more, or any combination of operations selected from

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the group consisting of gaseous or liquid fractional deposition, distillation, filtration, selective chemical vapor deposition (hereinafter CVD), settling, selective oxidation, selective halogenation, selective dissolution and selective extraction, and more preferably by means of gaseous fractional deposition.

Optionally, when desired, the separation stage may be followed by a purification procedure for each of the separated products, to remove impurities therefrom.

Optionally, a portion of the heat energy possessed by the product material of the primary heat treatment may be used in the halogenation, e.g., said product of the primary heat treatment may be transferred from the primary heat treatment chamber to the halogenation chamber when hot, and the halogenation reaction may be started shortly afterwards, and thus it is required to heat the material of the halogenation reaction merely from the temperature which it is at, and is substantially higher than, e.g., room temperature.

Optionally, the activation of metals in the halogenation reaction may be catalyzed by the introduction of the carbon produced during the primary heat treatment and/or of untreated flue-gas including e.g. bromine,

carbon, CO, CO<sub>2</sub> and SO<sub>x</sub> and NO<sub>x</sub> compounds from the primary heat treatment chamber into the halogenation chamber.

The present invention further relates to an apparatus by which such a recovery process is performed, which comprises a primary heat treatment chamber, a halogenation chamber and a separation unit; said primary heat treatment chamber comprises a waste inlet, a flue-gas outlet and means of heating, and is preferably connected to said halogenation chamber by means of a conduit, which comprises a valve; and said halogenation chamber comprises a means of controlled heating, a halogen compound inlet and optionally one or more outlets to withdrawn gas, liquid or solids therefrom; said apparatus further comprises a separation system comprises one or more of the following units, or any combination thereof, selected from the group consisting of fractional deposition unit, distiller, filter, CVD unit, settler, selective oxidation chamber, selective dissolution unit and selective halogenation system; said unit or units optionally being in contact with the outlet of said halogenator by means of a conduit.

Preferably, said separation system is a gaseous fractional deposition system and is connected to the outlet of said halogenator, by means of a conduit.

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Preferably, said fractional deposition system comprises one or more deposition columns wherein each column comprises means of maintaining the temperature thereof at a pre-determined level; said fractional deposition system further comprising an outlet pipe.

According to another preferred embodiment of the present invention, the separation system is a CVD system comprising one or more heated or chilled elements allowing the deposition of the specific metal halide vapors thereon.

Preferably, said outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber.

Optionally, said apparatus further comprises one or more units which can perform one or more actions selected from any of the group which consists of shredding, crushing, milling, sludge briquetting, feeding and dosing or any combination thereof, said unit being connected to the inlet of said primary heat treatment chamber and/or to the inlet of said halogenation chamber by means of a conduit.

Preferably, said apparatus further comprises an additional heat chamber, referred to hereinafter as secondary heat chamber, a heat exchanger, a scrubber a filter, a blower and a stack; said additional heat chamber

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comprising a means of heating, a gas inlet and an air inlet, and a flue gas outlet; said gas inlet of said secondary heat chamber being connected by means of a conduit to the flue gas outlet of said primary heat chamber; said heat exchanger comprising an inlet and an outlet; the flue gas outlet of said secondary heat chamber being connected by means of a conduit to the inlet of said heat exchanger; said scrubber comprising an inlet and an outlet; the outlet of said heat exchanger being connected, by means of a conduit to the inlet of said scrubber;

Preferably, said apparatus further comprises a filter, a blower and a stack; said filter comprising an inlet and an outlet; the outlet of said scrubber being connected, by means of a conduit to the inlet of said filter; said blower comprising an inlet and an outlet; the outlet of said filter being connected, by means of a conduit to the inlet of said blower; said stack comprising an inlet and an outlet; the outlet of said blower being connected, by means of a conduit to the inlet of said stack.

Preferably, said scrubber and said filter are connected to the halogenation chamber by means of conduits, to recycle material recovered and collected by said scrubber and filter to said halogenation chamber.



## DESCRIPTION OF THE INVENTION

The present invention relates to a high efficient process for the treatment of wastes which is applicable in treating mixtures of waste. Said mixtures consisting of a very wide range of chemical elements and compounds, organic and non-organic, in different physical forms, such as solid, liquid and gas. Said process comprises the following steps:

a) Primary heat treatment of the waste:

Said stage optionally includes evaporation of water, evaporation and carbonization of organic matters from the waste in a controlled oxygen atmosphere preferably at a temperature of less than 1000°C, or in metallic molten bath, said bath preferably being at a temperature of between 500°C and 1600°C. In the presence of hazardous waste, a secondary combustion chamber will destroy all remaining organic matters in the flue gas at a temperature of more than 1200°C at minimum of 2 seconds retention time. The primary heat treatment is conducted at a controlled oxygen level, thus, it may produce controlled and reduced metallic oxides and exchange or reduce the oxygen layer with carbon, and produce carbon residue which acts both as a catalyst in the halogenation reaction and impregnates into a portion the metal phase at elevated temperature which all will facilitate the halogenation reaction.

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In order to improve the productivity of the process according to the present invention and to render it ecologically friendly; the flue gas evolving from said primary heat treatment, which typically contains certain amounts of low temperature vaporized material, is subjected to an air purification procedure, according to techniques known in the art, which are preferably selected from scrubbing and filtration, to recover the desired materials from the flue ash, which materials are recycled and processed in the subsequent halogenation stage.

b) Halogenation of the product of the heat treatment:

Material present in the remainder of the waste and optionally, from other sources as well, and in particular, recycled material obtained upon recovering the flue gas by scrubbing and filtration, as described above, which may include metals, metal carbides, metal oxides, other inorganic material and possibly traces of organic material is halogenated at a temperature between- ambient temperature and 1500°C, preferably between 300°C and 1500°C, and more preferably between 700°C and 750°C. The carbon remaining in the waste, together with additional carbon, if required, acts as a catalyst in the halogenation. Preferably, the halogenation reaction is a chlorination reaction, a bromination reaction or a combined chlorination-bromination reaction, and more preferably the halogenation reaction is a chlorination reaction. Preferably, all of the above halogenation reactions are preformed in the gaseous phase.

The halogenation reaction may be conducted with various mechanical apparatus such as fluidized bed, vibrating grid, walking grid, rotary kiln and multi chamber.

The primary heat treatment chamber and/or the halogenation chamber of the present invention may be each independently be placed horizontally, vertically or in an angle.

According to one preferred embodiment of the present invention, hereinafter referred to as "selective halogenation", the halogenation reaction is carried out at a first temperature at which only some of the waste materials undergo reaction with the halogen, and upon separating the halides obtained, the temperature is varied and the halogenation of the remaining waste materials is completed, or partially completed, at a second temperature. If desired, the temperature is further varied and the procedure is repeated as many times as required. According to another preferred embodiment, the halogenation reaction is conducted at a temperature at which the halides are obtained in different states of matter, e.g., at a temperature in which one or more halides is a gas, and one or more of the other halides is a liquid or solid. One skilled in the art will appreciate that in the two embodiments described above, the halogenation temperature is an important parameter playing a role in accomplishing the separation of the halide products.

c) Separation of the halide products: such a separation can be preferably done by means of any one or more, or any combination of separations selected from the group consisting of gaseous or liquid fractional deposition, distillation, filtration, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution, selective extraction, selective chemical vapor deposition, selective electrical behavior and more preferably by means of gaseous fractional deposition (see, e.g. Zelickman A.N. Nikitina L.L. Moscow 1978).

Gaseous fractional deposition may be performed passing all the volatile chlorides,  $M_xCl_y$ , through one or more solidifying columns. Each has a temperature controlled system that maintains accurate conditions of e.g. temperature. The halide with the highest solidifying temperature solidifies in the first column, whereas the remainder of the halides in the gaseous phase pass to the next columns for further solidifying. In each solidifying column, there will be one or more definite halide materials. The resolution of the separation depends on the accuracy of the solidifying temperature and pressure control, and the dynamics of the gaseous flow. The solidified halides of each column may consist of the solidifying of several halides which are further separated, preferably by recycling each group of halides solidified in a certain column to the gaseous fractional deposition system, wherein accurate conditions are used to improve the resolution of the

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separation of the halides which have relatively close solidification temperatures. The substantially definite halides obtained thereby are subsequently preferably purified, to remove impurities therefrom. The final separation and purification steps may be accomplished using known technologies of hydrometallurgy and others, such as forming a solution in water or other liquids and filtration, solidification, CVD, etc. (see, e.g. Zehickman A.N. Nikitina L.L. Moscow 1978)

According to a preferred embodiment of the invention, the separation of the halide products comprises selective halogenation, selective evaporation and selective condensation, in any suitable sequence order and as many sequences as required. According to one preferred embodiment, the halogenation is carried out at a first temperature at which only some of the waste materials are converted to halides (selective halogenation), which halides, at said first temperature, are preferably in different states of matter, e.g., some halides are in the vapor phase while others are in a condensed phase (selective evaporation). The evaporated halides are removed from the reaction mixture, and are subsequently separated, preferably using the differences in their condensation temperatures, e.g., by gaseous fractional deposition (selective condensation) and optionally, additional methods known in the art. The reaction mixture, comprising non-evaporated halides together with waste materials which were not halogenated at said first temperature, such as glass and ceramics, is

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subjected to another separation procedure, to separate the non-evaporated halides therefrom, using methods known in the art, for example, methods based on the differences between the water solubility of said non-evaporated halides and the non-halogenated waste materials. Finally, the non-halogenated waste materials are reacted with halogen at a second temperature, preferably between 900-1500 degrees, or are separated by known hydrometallurgy technologies (see, e.g. Zelickman A.N. Nikitina L.L. Moscow 1978).

Optionally, the raw waste and/or the product of the primary heat treatment is mechanically prepared in a process which includes any one or more of the following steps:

- i) mechanical shaping of solid waste into pieces of a size to suit further equipment and productivity.
- ii) crushing and/or milling of waste;
- iii) briquetting of sludge

According to one embodiment of the present invention, a mixture of 1%-7% bromine in chlorine is used in the halogenation stage in the event that noble metal atoms or compounds such as Ag, Pt and Pd are present.

It is preferable to execute the primary heat treatment at a low as possible temperature in order to substantially reduce the evaporation of metals at said stage and thus reduce particle emission and to obtain an improved recycling efficiency.

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During the process of the present invention it is desirable to control parameters such as temperature of primary heat treatment and of halogenation, mass flow to, from and in the primary heat treatment chamber and halogenator in order to achieve higher efficiency. Thus, the waste movement into and in the primary heat treatment chamber may be adjusted in order to improve evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material and reduction of metal oxides mechanical reduction of the waste. The temperatures in the primary heat treatment chamber may be adjusted in order to obtain more efficient reaction with carbon, and its diffusion; the waste movement in the halogenator may be adjusted in order to achieve more efficient halogenation; the air flow in the primary heat treatment chamber may be adjusted in order to achieve an optimal carbonization, organic destruction, cracking, metal oxide reduction and halogenation. The chlorination chamber temperature may be adjusted in order to evaporate material having low boiling point or sublimation point and later material having higher boiling point or sublimation point, thus performing separation thereof.

Furthermore, the air flow in to the primary heat treatment chamber may be regulated in order to produce carbon in quantities required for optimal halogenation.

An advantage of carbonization resulting in incomplete combustion over that resulting in complete combustion is that the former results in less gasses than the latter, most of the organic matter is cracked into carbon and hydrogen molecules, the formation of CO and CO<sub>2</sub> molecules is substantially reduced. The gas flow in incomplete combustion is reduced in temperature, volume and velocity, which substantially reduces the particle emission and simplifies the treatment of the flue gas which consists of heat exchanging, heat recovery and emission control. The lower temperature reduces the amount of volatile inorganic matter in the flue gas. The lower velocity of the gas flow reduces the amount of particles drawn. The substantial reduction of in-flow of air usually required for said incomplete combustion can reduce the amount of emitted flue gas. The volatile organic matter only, can be further incinerated in the secondary chamber, however, said gas will require less oxygen for its incineration and will be almost free of non-gaseous particles. All the above renders the system more environmental friendly especially regarding the "greenhouse effect".

In the event that any of the various fractions of the metal halides which were deposited in the fractional deposition contains a mixture of halides, said mixture may be further separated and purified by known hydrometallurgy technologies and by further fractional deposition of higher resolution.



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Most of the waste is recycled by decomposing the material to its basic elements or their halide / oxide derivatives.

The process of the present invention being self-catalyzed, requires little or no addition of material for the purpose of catalysis. According to the present invention, use as catalysts in the recycling phase, is made of elements which exist in most of the wastes to be treated, thus the introduction of catalysts *per se* to the process is minimized.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 schematically illustrates an apparatus for a high efficient process for the treatment of multi-element wastes according to the present invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

According to one embodiment of the present invention, the scrap to be treated is inserted to a shredder, 1, and shredded therein. The shredded scrap is loaded by means of a ram loader, 2, into the rotary heat treatment chamber, 3, and the primary heat treatment is performed therein. The gaseous material exiting the primary heat treatment chamber flows to the secondary combustion chamber, 5, where all matters are combusted at an elevated temperature. Additional air is introduced through regulated vent (17). The hot flue gas flows to the heat exchanger (8) into which water is introduced through conduit (7) and withdrawn as a hot stream through

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conduit (18). The chilled flue gas passes through scrubber (6), where any gaseous emission is absorbed by caustic or lime. The flue gas further passes through the filter bag (4), to remove any particles. The filtered flue gas is released to the atmosphere by means of blower (19), through stack (20). The formation of high pressure within the system is prevented by means of valve (17) and blower (19). The non-gaseous material remaining from the primary heat treatment and the material recovered by the air purification procedure, i.e., the particles collected in the filter bags and the scrubber residues, are introduced into the halogenation chamber, 9, through valve, 21, which is closed during the halogenation reaction. Halogen compounds such as chlorine, bromine or a mixture thereof are introduced to the halogenation chamber via conduit 10. Condensation columns 11, 12, 13, 14 and 15 are maintained accurately at temperatures  $T_1$ ,  $T_2$ ,  $T_3$ ,  $T_4$  and  $T_5$ , accordingly, under the condition that  $T_1 > T_2 > T_3 > T_4 > T_5$ , and at an accurately controlled pressure. The gaseous product of the halogenation reaction is passed through said condensation columns, and the metal halides deposit thereon according to their characterized deposition temperature, and are collected and thus separated. The remaining gas which comprises excess halogen gas exits the apparatus through conduit 16. The non-gaseous material which remained in the halogenation chamber is collected and separated if required. Said remaining gas of the halogenation reaction may be recycled back into the halogenation chamber.

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According to a preferred embodiment of the present invention metal scrap/waste is reduced to a size that can be introduced to the equipment. Organic waste is treated in a controlled atmosphere or in a molten metallic phase with an oxygen deficiency in order to maintain carbon particles which will serve as catalysts and also reduce the oxide layer on the metallic waste. The gas streams pass through an air-controlled abatement system. The heated inorganic waste or the molten mixture with carbon, if necessary, are then fed to a halogenation reactor either - vertical, horizontal, fixed or fluidized bed. Additional carbon is introduced if needed. The carbon residue from the incineration process is used as a catalyst for the halogenation process.

According to a preferred embodiment, most of the metallic scrap is oxidized after a certain time of being exposed to the air, humidity and sun. This causes a problem to the extent that the oxide layer acts as a passive layer which deactivates the chlorination process. Said problem can be solved according to the present invention by the controlled incineration with oxygen deficiency at elevated temperatures of between 300°C and 1050°C, preferably between 800°C and 850°C. Thus, in the presence of a sufficient amount of carbon in the incinerator, the metal oxides and carbon may be converted to metals and CO and CO<sub>2</sub> according to the following empirical formula:



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According to a preferred embodiment the hot gas from secondary combustion chamber may pass through a heat recovery system namely a waste heat boiler, in which the energy is converted into steam and may produce electrical energy.

According to a preferred embodiment, use is made of bromine and/or bromine derivatives to accelerate chlorination of metals, especially noble metals.

According to one preferred embodiment, a portion of the flue gas exiting the primary heat treatment chamber or a portion of the flue gas exiting the secondary heat chamber are introduced to the halogenation chamber. Thus, oxygen or catalysts such as  $\text{SO}_x$ ,  $\text{NO}_x$  and/or carbon compounds, may be recycled.

According to a preferred embodiment of the present invention, the gas flow resulting subsequent to the fractional deposition process, which contains a high percentage of halogen gas, may be recycled back into the halogenator.

### EXAMPLES

#### Example 1

500 Grams of unsorted automobile scrap was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a length of approximately 10mm. Said pieces were carbonized (in the

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absence of oxygen) at a temperature of between 600°C-700°C for about 1 hour. Table 1 shows the content of said scrap before and after carbonization.

NAME	ELEMENT CONTENT (wt%)											
	Fe	Al	Cu	Ni	Mg	Co	Sn	O	Organic	noble metal	Wgt	%
Scrap before carbonization	53	18	4	2	4	1.5	1.3	5	11	0.05	500	100
Scrap after carbonization	61	21	4.5	2.0	4.6	1.7	1.5	-	2.4 carbon	0.05	432	86.4

Table 1

The carbonized material was further chlorinated at a temperature of about 750°C, and the various metal chlorides were separated. Table 2 shows the content of the material after the chlorination reaction .

ELEMENT CONTENT (%)										
Weight (gr.)	FeCl <sub>3</sub>	AlCl <sub>3</sub>	SnCl <sub>4</sub>	NiCl <sub>2</sub>	CuCl	CoCl <sub>2</sub>	noble metal	MgCl <sub>2</sub>	Condens. Chamber	Condens. Temp(°C)
	771			0.18					II	250-300
		440							III	1000
			14.2						IV	50
				14.5					I	600
130	4.26			3.5	28.5	15	0.46	78.3	V	
total: 1370	775.26	440	14.2	18.18	28.5	15	0.46	78.3		

Table 2Example 2

600 Grams of crushing electronic scrap was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a

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length of approximately 10mm. Said pieces were carbonized (in the absence of oxygen) at a temperature of between 650°C-700°C for about one hour.

Table 3 shows the content of said scrap before and after carbonization.

NAME	Cont. Element %													
	Fe	Cu	Ni	Sn	Pb	Zn	Co	As	Ag	Pd	O	Org.	C	Wt
Scrap before Carbonization	6	20	2.5	5.0	2.0	3.0	0.25	0.025	0.15	0.018	6	56	-	600
Scrap after Carbonization	13	44	5	11	4.4	6.6	0.5	0.055	0.33	0.04	-	2.5	4.0	270

Table 3

The material treated by means of primary heat treatment was chlorinated at a temperature of about 250°C for about 3 hours, and the various metal chlorides were separated. Table 4 shows the content of the material after the chlorination reaction.

NAME	Wgt.	FeCl <sub>3</sub>	SnCl <sub>4</sub>	NiCl <sub>2</sub>	ZnCl <sub>2</sub>	CoCl <sub>2</sub>	CuCl	PtCl <sub>2</sub>	AsCl <sub>3</sub> g/t	Ag g/t	Pd
Chloride iron FeCl <sub>3</sub>		101									
Chloride Tin SnCl <sub>4</sub>			61.0								
Chloride Nickel NiCl <sub>2</sub>				23							
Chloride Zinc ZnCl <sub>2</sub>					32						
Residue in Chlorinator	198			5.0	3.5	2.7	173	14.2	0.061 %	0.17%	0.058%
Total	415	101	61.0	23	35.5	2.7	173	14.2			

Table 4

Example 3

200 Grams of mixture of spent catalyst waste were introduced to the process of the present invention as follows: Said waste was treated by means of primary heat treatment, in the absence of oxygen, at a temperature of about 650°C for about 1.5 hours. Table 5 shows the content of said waste before and after primary heat treatment.

NAME	Cont. element %								
	Weight total	WO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Co <sub>2</sub> O <sub>3</sub>	Organic	C	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Scrap before Calcination	200 gr	38	9	31.0	3.5	20	-	24	14
Scrap after Primary heat treatment	100	W 31	Ta 7	31.0	Co 2.2	-	4.5	16	8

Table 5

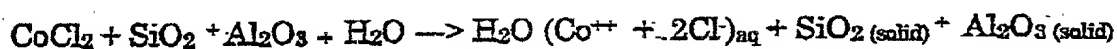
100 Grams of the calcinated material were chlorinated at a temperature of about 700°C, for about 2 hours, and those from among the various metal chlorides which were evaporated at said temperature, were removed from the reaction mixture and subsequently separated in condensation columns, due to the differences in their condensation temperature. Table 6 shows the content of the material after the chlorination reaction. Alternatively, the evaporated metal chlorides may be all condensed at 20°C on one column, and may be subsequently separated upon raising the column temperature, due to their differences in their evaporation temperature.

NAME	Weight	WCl <sub>5</sub>	TaCl <sub>5</sub>	TiCl <sub>4</sub>	CoCl <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Halog. T °C)	Evapo. T °C)	condens. T °C)
WCl <sub>5</sub>		64						650	350	200-250
TaCl <sub>5</sub>			9.0					650	240	200-250
TiCl <sub>4</sub>				122				450	136	0-20
CoCl <sub>2</sub>					4.6			500	900	500
SiO <sub>2</sub>						14		900	950	500
Al <sub>2</sub> O <sub>3</sub>							6.8	900	950	500
Residue in Chlorinator	25.0				4.6	14	6.8			
Total	245	64	9.0	122	4.6	14	6.8			

Table 6

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The remaining residue in the chlorinator comprised a non-evaporated halide ( $\text{CoCl}_2$ ) and two oxides, which did not undergo chlorination at  $700^\circ\text{C}$ . The  $\text{CoCl}_2$  was separated from  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , e.g. according to the principle of differences of solubility in water as described in the following equation:



The remaining  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were introduced to a chlorination chamber at  $950^\circ\text{C}$  and were converted to  $\text{AlCl}_3$  (18g) and  $\text{SiCl}_4$  (32g).

#### Example 4

The primary heat treatment of Example 3 was repeated, and 100g of the material treated by means of primary heat treatment was chlorinated at a temperature of about  $900^\circ\text{C}$ , for about 1.5 hours, and the various metal chlorides were separated. Table 7 shows the content of the material after the chlorination reaction.

NAME	Weight	$\text{CoCl}_2$	$\text{WCl}_6$	$\text{TaCl}_5$	$\text{AlCl}_3$	$\text{TiCl}_4$	$\text{SiCl}_4$
Chloride Cobalt - $\text{CoCl}_2$		4.7					
Chloride Tungsten - $\text{WCl}_6$			64				
Chloride Tantalum - $\text{TaCl}_5$				9.0			
Chloride Aluminum - $\text{AlCl}_3$					18		
Chloride Titanium - $\text{TiCl}_4$						122	
Chloride Silicon - $\text{SiCl}_4$							32
Residue	6.0				$\text{Al}_2\text{O}_3$ 2.5		$\text{SiO}_2$ 8.5

Table 7

#### Example 5



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A mixture of 100g of Nickel-Cadmium batteries was introduced to the process of the present invention as follows: At first said scrap was shredded to pieces of a length of approximately 1-5cm. Said pieces were calcinated (in the absence of oxygen) at a temperature of about 650°C, for about 3 hours. Table 8 shows the content of said scrap before and after primary heat treatment.

Type of scrap	% Ni	%Cd	%Fe	% Organic Silicon
Before Primary heat treatment	20	14	32	34
After Primary heat treatment	24	16	34	SiO <sub>2</sub> - 16; C - 20

Table 8

The material treated by means of primary heat treatment was chlorinated at a temperature of about 650°C, for about 1.5 hours, and the various metal chlorides were separated. Table 9 shows the content of the material after the chlorination reaction.

NAME	Weight	FeCl <sub>3</sub>	NiCl <sub>2</sub>	CdCl <sub>2</sub>	SiO <sub>2</sub>	C
Chloride Iron FeCl <sub>3</sub>		96				
Chloride Nickel NiCl <sub>2</sub>						
Chloride Cadmium CdCl <sub>2</sub>						
Residue in Chlorinator	101		49	26	16	10

Table 9

While some embodiments of the invention have been illustrated, it will be clear that the invention may be carried out by persons skilled in the art with many modifications, variations and adaptations, without departing from its spirit or exceeding the scope of the claims. Thus, e.g., the invention may be applied to scrap or apparatus different from that herein described.

CLAIMS

1) A high efficient recovery process for the treatment of multi-element wastes which comprises the steps of

- a) heat treatment of the waste in the presence of a controlled amount of oxygen;
- b) halogenation of the product of step "a"; and
- c) separation of the metal halide products of step "b".

2) A process according to claim 1 in which said multi-element waste is unsorted.

3) A process according to claim 1 in which the waste to be recovered is such that has been mechanically prepared in a process which includes any one or more of the steps of shredding, crushing, milling and briquetting.

4) A process according to claim 1 in which said primary heat treatment further comprises mechanically agitating the waste during said treatment.

5) A process according to claim 1 in which the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material,

carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

6) A process according to claim 1 in which the primary heat treatment is carried out under atmospheric pressure or higher pressure, optionally in the presence of gases, preferably hydrogen, capable of cracking the organic or inorganic material.

7) A process according to claim 1 in which the halogenation reaction therein is selected from the group which consists of chlorination, bromination, or chlorination and bromination.

8) A process according to claim 1 in which at least a portion of the heat energy afforded in the primary heat treatment is used in the halogenation reaction.

9) A process according to claim 1 in which at least a portion of the product of the primary heat treatment is used as a catalyst in the halogenation reaction.

10) A process according to claim 9 in which said products to be used as catalysts are selected from the group which consists of carbon, bromine, carbon, CO, CO<sub>2</sub> and SO<sub>x</sub> and NO<sub>x</sub> compounds.

11) A process according to claim 1 wherein the primary heat treatment is performed in an oven.

12) A process according to claim 11 wherein said oven is at a temperature of less than about 1000°C.

13) A process according to claim 1 wherein the primary heat treatment is performed in a metallic molten bath.

14) A process according to claim 13 wherein said molten bath is at a temperature of between 500°C and 1600°C.

15) A process according to claim 1 which further comprises a secondary heat treatment comprising heating the gaseous flow which results from the primary heat treatment to a temperature of more than 1200°C.

16) A process according to claim 1 in which said halogenation step further comprises mechanically agitating the waste during said step.

17) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between ambient temperature and 1500°C.

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18) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between 300°C and 1500°C, and preferably between 700°C and 750°C.

19) A process according to claim 1 in which the waste comprises a substantial percentage of any of the metals selected from the group which consists of Ag, Pt and Pd, and the halogenation reaction is performed by using a mixture of bromine and chlorine.

20) A process according to claim 19 in which said mixture of chlorine and bromine comprises between 93% and 99% chlorine and the remainder is bromine.

21) A process according to claim 1 in which at least a portion of the excess halogen gas remaining from the halogenation reaction is recycled back to the halogenation chamber.

22) A process according to claim 1 in which the separation of the metal halides is by means of any one or more of the group selected of gaseous or liquid fractional deposition, distillation, fractional distillation, filtration, selective chemical vapor deposition, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution and selective extraction.

23) An apparatus for a high efficient recovery process for the treatment of multi-element wastes, which comprises a primary heat treatment chamber, a halogenation chamber and a separation unit; said primary heat treatment chamber comprises a waste inlet, a flue-gas outlet and means of heating; said halogenation chamber comprises a means of heating, a halogen compound inlet and an outlet.

24) An apparatus according to claim 23 in which the flue-gas outlet of said primary heat treatment chamber is connected to said halogenation chamber by means of a conduit, which comprises a valve.

25) An apparatus according to claim 23 in which said separation system comprises one or more of the units selected from the group which consists of fractional deposition unit, distiller, filter, settler, selective chemical vapor deposition unit, selective oxidation chamber, selective halogenation chamber, evaporation chamber and selective dissolution unit or any combination thereof.

26) A apparatus according to claim 25, wherein the separation system comprises fractional deposition unit or selective chemical vapor deposition unit.

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27) An apparatus according to claim 25 in which said separating unit is in contact with the outlet of said halogenator by means of a conduit.

28) An apparatus according to claim 23 in which said separation system is a gaseous fractional deposition system; the inlet of which is connected to the outlet of said halogenator, by means of a conduit.

29) An apparatus according to claim 28 in which the outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber, and said pipe comprises a one-way valve in the direction from the fractional deposition system to the halogenation chamber.

30) An apparatus according to claim 23 which further comprises an additional heat chamber and a heat exchanger; said additional heat chamber comprising a means of heating, a gas inlet, an air inlet, and a flue gas outlet; said gas inlet of said additional heat chamber being connected by means of a conduit to the flue gas outlet of said primary heat chamber; said heat exchanger comprising an inlet and an outlet; the flue gas outlet of said additional heat chamber being connected by means of a conduit to the inlet of said heat exchanger.

31) An apparatus according to claim 30 which further comprises a scrubber, a filter, a blower and a stack; said scrubber comprising an inlet and an

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outlet; the outlet of said heat exchanger being connected, by means of a conduit to the inlet of said scrubber; said filter comprising an inlet and an outlet; the outlet of said scrubber being connected, by means of a conduit to the inlet of said filter; said blower comprising an inlet and an outlet; the outlet of said filter being connected, by means of a conduit to the inlet of said blower; said stack comprising an inlet and an outlet; the outlet of said blower being connected, by means of a conduit to the inlet of said stack.

32) An apparatus according to claim 31, wherein the scrubber and the filter are connected to the halogenation chamber by means of conduits, to recycle material recovered and collected by said scrubber and filter to said halogenation chamber.

33) An apparatus according to claim 31 in which said filter is selected from the group which consists of fabric filter, electrostatic filter, and high temperature filter.

34) An apparatus according to claim 25 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter doser, and sludge feeder, which are connected to the primary heat treatment chamber; providing that the outlet of the unit connected to the primary heat treatment chamber is connected to the inlet of said primary heat treatment chamber by means of a conduit; further



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providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

35) An apparatus according to claim 23 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter, doser and sludge feeder which are connected between the primary heat treatment chamber and the halogenation chamber; providing that the outlet of the unit which is connected to the halogenation chamber is connected to the inlet of said halogenation chamber by means of a conduit; further providing that the outlet of the primary heat treatment chamber is connected to the inlet of the unit which is connected to said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

36) An apparatus according to claim 23 in which said primary heat treatment chamber further comprises a means of agitating material.

37) An apparatus according to claim 36 in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

38) An apparatus according to claim 23, wherein the primary heat treatment chamber comprises a pressurized vessel.

39) An apparatus according to claim 23 in which said halogenation chamber further comprises a means of agitating material.

40) An apparatus according to claim 39, in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

41) An apparatus according to claim 23, wherein the halogenation chamber comprises a pressurized vessel.

42) An apparatus according to claim 23, in which the primary heat treatment chamber is placed horizontally, vertically or at any other advantageous angle.

43) An apparatus according to claim 23 in which the halogenation chamber is placed horizontally, vertically or at any other advantageous angle.

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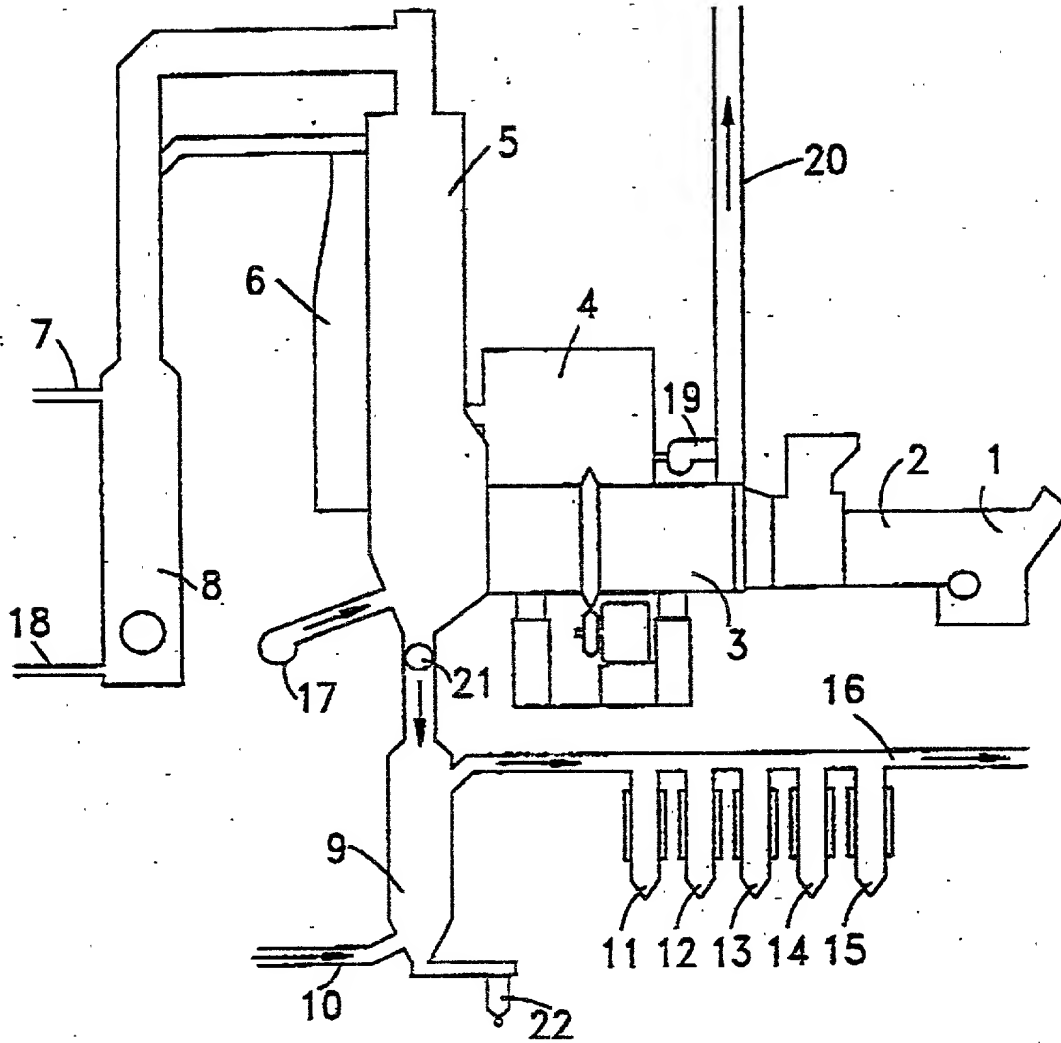


Fig. 1

## COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Includes Reference to PCT International Applications)

4297

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HIGH EFFICIENCY RECOVERY PROCESS AND APPARATUS FOR THE

PYROLYSIS TREATMENT AND HALOGENATION OF THE MULTI-ELEMENT WASTE

the specification of which (check only one item below):

☐ is attached hereto.

☒ was filed as United States application

Serial No. 09/601,062 ✓

on July 26, 2000 ✓

and was amended

on \_\_\_\_\_ (if applicable).

☐ was filed as PCT international application

Number \_\_\_\_\_

on \_\_\_\_\_

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

## PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Israel	123068	January 26, 1998 ✓	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

## Combined Declaration For Patent Application and Power of Attorney (Continued)

(includes Reference to PCT International Applications)

4297

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

## PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)		
PCT/IL99/00045	January 25, 1999			

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

Michael N. Meller - Registration No. 20779  
Eugene Lieberstein - Registration No. 24645

## Send Correspondence to:

Anderson, Kill & Olick, P.C.  
1250 Avenue of the Americas  
New York, NY 10020-1182

Direct Telephone Calls to:  
(name and telephone number)

Michael N. Meller, Esq.  
(212) 278-1229

201	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
202	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
203	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201

SIGNATURE OF INVENTOR 202

SIGNATURE OF INVENTOR 203

DATE

DATE

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